Title:

"Desulphurization of ferrous materials using glass cullet"

Cross-reference to related applications:

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Title:	
"Desulphurization of ferrous materials using sodium silicate"	
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Description

FIELD OF THE INVENTION

The present invention relates to (1) the use of glass cullet as the primary desulphurizing reactant in a reactive desulphurizing agent, (2) the option of including other desulphurizing reactants obtained from other reactive alkali oxides, alkaline oxides or other chemical compounds and metallic solids, (3) the application of a glass cullet based reactive desulphurizing agent to a molten ferrous material and (4) the deoxidation or reduction of the iron oxide in a molten ferrous material.

BACKGROUND OF THE INVENTION

Ample agreement exists on the growing need for low sulphur steels. In most types of steels, the presence of sulphur above 0.015% is undesirable. The increasing stringent requirement for better desulphurization of steel is attributed to the need for producing high strength low alloy steel and steels resistant to hydrogen induced cracking. In addition, even minute contents of sulphur has pernicious effects on the manufacturing and finishing of steel products, such as brittle fractures in welding and fabrication, a tendency to separate along grain boundaries when stressed or deformed at temperatures near the melting point during the hot rolling phase in sheet steel processing, and even the influences on as-cast and the processing characteristics of the steel in terms of the workability of surface finish.

The desulphurizing of molten ferrous materials comprises thoroughly permeating the molten material with a reactive desulphurizing agent consisting of (1) metal oxides for replacing the sulphur from the iron and for providing the flux required to float out the spent reactants and (2) the addition of solid metals to complete the deoxidization or reduction the iron. U.S. Pat. No.

4,014,685 teaches the four essential factors, for achieving good desulphurization in either a molten iron or steel, using a reactive desulphurizing agent. The factors are (1) high desulphurizing agent basicity, (2) high temperature on desulphurizing agent contact with the molten material, (3) low oxygen potential and (4) high desulphurizing agent fluidity.

Over the past several decades, a multitude of methods and processes have been set forth for the desulphurization of ferrous molten materials. Most of these methods are based on the reactions of a lime, fluorspar, aluminum oxide, alkali and alkaline metals or alloys, as well as the use of other reactants. An example of these methods is in U.S. Pat. No. 3,779,739, which teaches the art of desulphurization using calcium oxide and aluminum oxide or calcium oxide and calcium fluoride, wherein the calcium oxide increases the basicity of the desulphurizing agent and the aluminum oxide and calcium fluoride increase the fluidity of the desulphurizing agent. Magnesium oxide has also been advanced in the art of desulphurizing ferrous materials, specifically metallic magnesium in U.S. Pat. No. 6,383,249.

Sodium, like magnesium, is a highly reactive metal, thus a high-performing desulphurizer that allows for a very high sulphur replacement in molten ferrous materials. However, because of its high reactive property, metallic sodium is highly unstable at ambient temperatures and violently reactive at the temperatures of molten ferrous material and thus would vaporize explosively on contact with molten ferrous materials, hence metallic sodium, by itself, is ineffectual as a desulphurizer. A preferred composition for the effective use of sodium as a desulphurizer is a chemical compound, such as in an oxidized state in combination with a flux-enhancing compound. A far-reaching attractive feature in advancing the art of using sodium over magnesium as a desulphurizer is the availability of sodium compounds at a significantly lower cost.

The art of using sodium oxide, derived from sodium carbonate, as a stable reactant in a desulphurizing agent is described in U.S. Pat. No. 4,014,685, U.S. Pat. No. 4,956,010, and U.S. Pat. No. 4,353,739. In none of these examples, where the art of using sodium oxide as a reactant in a reactive desulphurizing agent is put forth, is the art advanced wherein glass cullet is used as the source of the sodium oxide desulphurizing reactant. Nor is a mention made on the preferred form for using a glass cullet composition as the sole desulphurizer reactant in a desulphurizing agent.

Glass cullet is a ubiquitous waste product and is derived primarily from the recollection of glass from homes, business and industries. Fundamentally, glass is an amorphous mixture of silicon dioxide with alkaline and alkali metal-earth oxides and other materials, wherein sodium oxide is one of them. The silicon dioxide, however, forms the structural network for all glasses. The most commonly produced glass is the soda-lime glass. Typically, soda-lime glass contains about 73% of SiO_2, about 17% of Na_2O, and about 5% of CaO and about 4% of MgO. Although, the silicon dioxide is the main stay for glasses, the desirable physical properties of the glass composition are derived from the combined effects of the remaining oxides in the composition. One of these properties is the softening or melt point.

By itself, the melt point of SiO_2 is about 1580°C. However, once the SiO_2 is mixed or combined with other oxides to form a glass, the melt point of the resulting composition is much lower. In the case wherein the composition is a soda-lime glass, the melt point is around 700°C. The low melt point of the soda-lime glass renders an important practical and industrial property, the feasibility of being handled at lower temperatures. Because of its lower-temperature workability, glass is widely used in large amounts in the production of bottles, jars, everyday drinking glasses, and windowpane glass. All these glass products have a high index of

recoverability; hence a plentiful and replenishable source of low-cost glass cullet is widely available for the desulphurization of ferrous materials.

The lower melt point of glass is an added attractive feature when glass cullet is used as a reactive desulphurizing agent. On contact with the molten ferrous material, less thermal energy is required to dissolve the solid glass cullet reactive desulphurizing agent; thus, less caloric energy is necessary to maintain the ferrous material in its molten state as the sulphur replacement progresses. Hence, the use of glass cullet as a desulphurizing agent is an efficient and effective method for removing sulphur from ferrous materials.

SUMMARY OF THE INVENTION

A method is disclosed for removing sulphur in molten ferrous materials using a sodium-based as a reactive desulphurizing agent. The preferred source for the sodium-based reactive desulphurizing agent is glass cullet. A lime, dolomite, an alumina or mixtures thereof, may optionally be added to enhance the replacement of the sulphur and control of the fluidity of the spent reactants in the molten ferrous materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a reactive desulphurizing agent is glass cullet, wherein the chemical composition of the glass cullet comprises of y parts of SiO_2 to x parts of Na_2O and wherein, yet further, the ratio, y/x, is anywhere from 0.5 to 5. The SiO_2 and the Na_2O in the glass cullet are in a fused solid state.

The glass cullet reactive desulphurizing agent is brought in intimate contact with sulphur-laced molten ferrous materials. In the preferred embodiment of the invention, the molten ferrous material is drawn, in a predetermined amount, and laid in a first layer to cover the surface of a

desulphurizing vessel. A layer of the glass cullet reactive desulphurizing agent, in a predetermined amount, is then laid to cover the first layer of the molten ferrous material. A second layer, of a predetermined amount, of the molten ferrous material is laid to cover the glass cullet reactive desulphurizing agent. The process is repeated at least once until all the molten ferrous material available is desulphurized within the volume capacity of the vessel. As the desulphurization of the molten ferrous materials progresses, the spent reactants fluidize the surface and are removed from the desulphurizing vessel.

Wide varieties of methods and means, apparent to those skilled in the art, are available for intimately combining the interactive desulphurizing agent with the molten ferrous material. One other such method comprises, wherein at least one first layer laid down in the desulphurizing vessel of the reactive desulphurizing agent, then followed by at least one layer of the molten ferrous material to cover the reactive desulphurizing agent. One other such means for combing the reactive agent with the molten ferrous material comprises the granulation of the solid interactive desulphurizing agent, suspending said granulation in an inert carrier gas and injecting said inert carrier gas with said suspended granulation into the interior of the molten ferrous material.

The reduction or deoxidation of the iron is accomplished by a reactive metallic solid introduced into the molten ferrous material. In the preferred embodiment of the invention the metallic solid is an aluminum rod. A number of deoxidizing metallic solids, known to those familiar with the art, are suitable for reducing the iron.

In another embodiment of the invention, the reactants of the reactive desulphurizing agent comprise: glass cullet, as prepared in the preferred embodiment, and oxides of calcium,

magnesium and aluminum. The preferred materials for said oxides are a lime compound such as limestone, dolomite and an alumina composite, respectively.

The said preferred reactive desulphurizing agent composition is combined with the molten ferrous materials, using the procedure as described in the preferred embodiment of the invention.

Na_2O	from about	7 to about 50%
SiO_2	from about	7 to about 50%
CaO	is	≤ 45%
MgO	is	≤ 8%
Al_2O_3	is	≤ 25%

These and other advantages and features of the present invention will be more fully understood with the examples thereof.

EXAMPLE 1

A reactive desulphurization agent, based on sodium, was prepared from a glass cullet and oxides of aluminum, magnesium and calcium. The glass cullet had a silicon oxide to the sodium oxide parts ratio composition of 2.3:1, resulting in about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. In addition to the glass cullet composition, anhydrous calcined materials: alumina, dolomite and lime, where added in the amounts given in Table 1. The components where combined using a blade mixer in three approximately equal batches to obtain consistent mixtures. The percentages based on weight (pbw) of the oxides for the unspent reactive desulphurizing agent are listed in Table 2. After mixing, the components were placed super-sacks and shipped to the site of the Basic Oxygen Furnace (BOF).

Table 1.

Desulphurizing Agent Component Weight	
Component	**Kg**
Glass cullet	234.5
Alumina	284.1
Dolomite	218.8
Lime	535.4
Total	**1272.8**

Table 2.

Desulphurizing Agent Composition (pbw)	
Reactive Oxides	**Percent by Weight**
CaO	53.33%
MgO	7.19%
Na_2O	5.70%
Flux Enhancers	**Percent by Weight**
Al_2O_3	18.35%
SiO_2	15.42%
Total	**100.00%**

At the BOF site, initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the glass cullet reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered the glass cullet reactive desulphurizing agent. The controls parameters were maintained constant to provide oxygen at 356ppm. A solid metallic aluminum wire was injected into the molten steel

to deoxidize the iron oxide, with the oxygen reduced to 2.5ppm. During the desulphurization of the molten steel, neither the presence of toxic vapors nor the presence of sodium where detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent remained dissolved and fluid during the desulphurization process. Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.012% to about 0.0088%.

EXAMPLE 2

In the second example, the sodium-based reactive desulphurizing agent based was again prepared from a glass cullet and oxides of aluminum, magnesium and calcium. The parts ratio of the silicon oxide to the sodium oxide was maintained as before, 2.3:1, resulting in a glass cullet composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. However the amounts the glass cullet composition, and the three anhydrous calcined materials: alumina, dolomite and lime, were slightly changed, as given by weight amounts in Table 3. As before, the components where combined using a blade mixer in successive separate batches. The individual batch weights for this example were not reported. The percentages based on weight of the oxide in the final sodium-based reactive desulphurizing agent composition are listed in Table 4. After mixing, the components were placed super-sacks and shipped to the BOF site.

Table 3.

Desulphurizing Agent Component Weight	
Component	**Kg**
Glass cullet	225.8
Alumina	364.8
Dolomite	200.9
Lime	408.5
Total	**1200.0**

Table 4.

Desulphurizing Agent Composition (pbw)	
Reactive Oxide	**Percent by Weight**
CaO	45.50%
Na_2O	7.00%
MgO	7.00%
Flux Enhancers	**Percent by Weight**
Al_2O_3	25.00%
SiO_2	15.50%
Total	**100.00%**

Essentially the desulphurization procedure at the BOF site, as outlined in Example 1, was repeated in this example, with the exception that the oxygen levels were lower both during the desulphurization phase and the deoxidation phase. Initially, 70 metric tons of molten steel were

drawn into a tap vessel and covered by 400 kg of the glass cullet reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered with a layer of the glass cullet reactive desulphurizing agent. The controls parameters were maintained constant to provide oxygen at 226ppm. Metal aluminum wire was injected into the molten steel to deoxidize the iron oxide. In this example, the oxygen was reduced to 1.7ppm. During the process, neither the presence of toxic vapors nor the presence of sodium where detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent, as before, remained dissolved and fluid during the desulphurization process. Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.0153% to about 0.0135%.

A further variation of the process consists of a number of sequential charges of lesser amounts of the molten steel charge and provide said molten charge with a layer of the reactive desulphurizing agent, wherein each layer of the reactive desulphurizing is in intimate contact with the molten material.

It will be appreciated, to those skilled in the art, that the instant specifications and claims are set forth by way of illustrating and not limiting the present invention, and that various modifications and changes may be made without departing from the spirit, scope and intent of the present invention.